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3 KEYWORDS: photocatalytic reaction, micro and nanomotors, visible light, active Janus particles,
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5 spherical colloidal particles, exclusion phenomena
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12 ABSTRACT. Synthetic nano- and micromotors interact with each other and their surroundings in
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14 a complex manner. Here, we report on the anisotropy of the active-passive particles interaction in
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16 a soft matter system containing an immobile yet photochemical Ag/AgCl-based Janus particle
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18 embedded in a dense matrix of passive beads in pure water. The asymmetry in the chemical
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20 gradient around the Janus particle, triggered upon visible light illumination, distorts the isotropy
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22 of the surrounding electric potential and results in the repulsion of adjacent passive beads to a
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24 certain distance away from the Janus particle. This exclusion effect is found to be anisotropic with
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26 larger distances to passive beads in front of the Ag/AgCl cap of the Janus particle. We provide
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28 insight into this phenomenon by performing the angular analysis of the radii of exclusion and track
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30 their time evolution at the level of a single bead. Our study provides not only a novel fundamental
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32 insight into the collective behavior of a complex mixture of active and passive particles, but is also
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34 relevant for various application scenarios, *e.g.* particles transport at micro- and nanoscale and local
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36 chemical sensing.
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INTRODUCTION

Interactions between species are very common in nature ranging from microorganisms up to mammals. The individual microorganisms in groups coexist driven by a common goal, e.g. to survive or achieve benefits. These groups typically exhibit complex behavioral patterns like schooling or grouping.¹ Characteristic examples include communication of individual cells and microorganisms with each other to form multicellular aggregates when lack of nutrients.² Similar to biological systems,^{3,5} the study of interactions between synthetic actively moving objects and their environment represents a dynamic research field.^{6,9} The interest is primarily motivated by the fact that synthetic nano- and microswimmers moving due to the conversion of chemical energy into mechanical motion¹⁰⁻¹⁸ can mimic numerous functions of natural systems. These artificial model systems have attracted strong attention due to their envisioned impact on life sciences, materials science and environmental research.¹⁹⁻²² The key goal is to achieve an efficient control of man-made microswimmers and understand their interaction with the microenvironment aiming to address a broad range of applications, ranging from MEMS and lab-on-a-chip systems through the accomplishment of complex tasks as nanomachinery, nanomedicine, all the way to (bio-) chemical sensing.²³⁻²⁶

Recent studies address different systems involving interactions between active particles,²⁷ active particles and passive beads,^{6,28-31} or active particles with a confinement potential, e.g. walls.³²⁻³⁴ The propulsion of active particles is often achieved by the designed asymmetry of their geometry, e.g. in the case of Janus particles³⁵⁻³⁶ their active side is used to form gradients of temperature,³⁷ chemical concentration,⁶ pressure,¹⁶ or electric potential.³⁸ Such gradients are typically long-ranged (up to several particle diameters d) and can lead to specific responses of the nearby objects, leading to

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3 emerging collective behavior like swarming, schooling,^{28,39} exclusion,⁴⁰ shape assembling,⁴¹ or those
4 resembling predator-prey interactions in nature.³⁹
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8 Rather complex interactions are observed in dense environments of interacting dissimilar
9 species, *e.g.* when active and passive objects are placed at distances comparable to their linear
10 dimensions. The proximity leads to a strong interaction between passive matrices and local
11 gradients generated by active particles. Similar processes are very common in nature. For instance,
12 "bacterial turbulence"⁴² is referred to a large-scale intermittent motion in the form of vortices and
13 can be achieved only at high cell concentration or spermatozoa that tend to form bundles to swim
14 more efficiently in viscous fluids.⁴³ Therefore, in-depth studies of synthetic interacting systems
15 using statistical approaches⁴⁴ help us to understand not only the competing interactions governing
16 the behavior of the system but also to explore the impact of active particles on dense environments.
17 In this respect, there has been considerable interest in the collective behavior of dense assemblies
18 of hard sphere-like active or self-propelled particles close to the glass transition,⁴⁴⁻⁴⁷ as well as the
19 phase behavior of a dense active suspension of self-propelled colloids.⁴⁸⁻⁴⁹ While dense systems of
20 passive beads and active particles are actively investigated, the *anisotropy in the particle-bead*
21 interactions in a dense matrix, (*e.g.* amorphous, glassy or crystal⁵⁰) still lacks even a
22 phenomenological description.
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42 Here, we study the anisotropy in the interaction of visible light-driven Ag/AgCl-based spherical
43 Janus particles embedded in a dense matrix of passive SiO₂ beads in pure water (Figure 1a). In
44 contrast to prior works,³⁵⁻³⁶ we consider the case when Janus particles are fixed to a glass substrate.
45 Therefore, we primarily track the dynamic properties of the surrounding passive beads. We
46 observe an anisotropic profile of the repulsive interaction between active Janus particles and
47 passive beads and explain it as a result of an asymmetry in the chemical gradient around the Janus
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3 particle, triggered upon visible light illumination. This leads to a distortion in the initially isotropic
4 surrounding electric potential and results in the asymmetric exclusion of passive beads around the
5 Ag/AgCl cap. We follow the time evolution of a spatial distribution of passive beads and analyze
6 their displacement around the Janus particle. We describe two limiting cases, when a Janus particle
7 is completely immobile, or when it can perform rotational but no translational motion. With this
8 study, we provide new insights into the rotational dynamics of photocatalytically active Janus
9 particles embedded in a dense matrix of passive beads. We anticipate that these phenomena,
10 peculiar for electro-kinetic motors, can only be observed due to the confinement imposed by a
11 dense environment.
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26 **EXPERIMENTAL**

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28 Photocatalytic Ag/AgCl spherical Janus particles are fabricated as have been demonstrated
29 elsewhere.³⁵⁻³⁶ In brief, monolayers of polystyrene spheres with a diameter of 2 μm are deposited
30 with a 60 nm thick layer of silver, which is converted to a silver chloride by placing capped
31 particles in a FeCl_3/PVP solution. Janus particles with the synthesized Ag/AgCl caps (Figure 1b)
32 are washed in deionized (DI) water using a centrifugation process and suspended in DI water for
33 further use.
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42 When illuminating such Janus particles with blue light (450 nm - 470 nm, intensity 137
43 $\mu\text{W}/\text{mm}^2$), they reveal self-propulsion (Figure S1).³⁵ This is attributed to the coupling of the
44 plasmonic light absorption by a Ag/AgCl cap⁵¹ and the efficient photochemical production of ions
45 at the cap structure.⁵² Namely, as a result of the photochemical reaction, AgCl is reduced to Ag
46 producing protons and chloride ions (Figure 1c). As protons have a significantly higher diffusivity
47 than chlorine ions ($D_{\text{H}^+} = 9.311 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ versus $D_{\text{Cl}^-} = 1.385 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), a local electric field
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3 is generated around the Janus particle.^{8, 28, 36, 53} This electric field is oriented inward, *i.e.* towards
4 the cap (Figure 1c).^{8, 54-55} The rate of the photochemical reaction is found to be time-dependent.
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6 This conclusion is done based on the analysis of the motile Janus particles where we observe
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8 individual active Janus particles moving with the initial average speed of 20 $\mu\text{m/s}$, which then
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10 gradually decreases down to 8 $\mu\text{m/s}$ in the next 20-50 s (Figure S1). A similar behavior with the
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12 exponential decay of the velocity with time was observed by Wang's group and is attributed to the
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14 self-consumption of AgCl.⁵⁴
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19 To understand how the dynamics of the passive matrix is affected by active particles, we fixed
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21 Janus particles on a substrate and then added a suspension of size-matched chemically inert silica
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23 beads. Under a reference white light illumination (light intensity of 1.3 $\mu\text{W}/\text{mm}^2$) passive beads
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25 display Brownian diffusion. Janus particles and passive beads interact via repulsive electrostatic
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27 interaction due to a similar negative zeta potential ($\zeta_{\text{Janus}} = -15.1 \pm 3.6 \text{ mV}$, $\zeta_{\text{silica}} = -38.7 \pm 0.9 \text{ mV}$). Once
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29 the blue light illumination is turned on (450 nm - 470 nm, intensity 137 $\mu\text{W}/\text{mm}^2$), the
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31 photocatalytic decomposition of AgCl at the cap of Janus particles locally releases charged species
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33 into the solution. The electric field pointing towards the Ag/AgCl cap acts electrophoretically on
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35 the negatively charged silica beads and generates their repulsion from the Janus particles.^{35-36, 54} We
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37 focus on the dynamics of surrounding passive beads that efficiently reflect the transient processes
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39 in the system.
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47 **RESULTS AND DISCUSSION**

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49 We consider two cases to address the effect of asymmetry in the exclusion behavior: (a) when
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51 active particles are fixed to the surface and can perform neither translational nor rotational motion,
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3 and (b) when only translational motion of the active particle is suppressed and a Janus particle can
4 rotate around its axis.
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10 **Active Janus particles are immobile**

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12 In this series of experiments, Janus particles are photocatalytically active but they do not perform
13 translational and rotational motion. The density of passive beads in this experiment is 0.151
14 particles/ μm^2 (Figure S2). Once the blue light is on, the repulsion between the Janus particles and
15 passive silica beads is initiated (Figure 1d-g, Video S1). The data clearly demonstrates that the
16 distance from the PS side of the Janus particle to passive beads is smaller than the distance from
17 the Ag/AgCl cap of the Janus particle. To address this asymmetry in the interaction process, we
18 focus on the analysis of several layers of passive beads around the Janus particle (within a circle
19 with a radius of about 12 μm) as those beads are mostly affected by the photochemical reaction.
20 The concentration of the products of the photocatalytic reaction in front and at the sides of the cap
21 of the Janus particle is high. There are no ions generated at the PS side of the Janus particle. Still,
22 diffusional processes form “tails of the distribution” and induce less pronounced repulsion between
23 the Janus particle and passive beads. For further quantitative analysis of the temporary evolution
24 of the system, it is insightful to split the dense matrix of passive beads into three different groups
25 according to their location with respect to the cap of the immobile Janus particle (Figure 1d and
26 Figure S3): in front of the Ag/AgCl cap (red, I), at the particle laterals (blue, II), in front of the PS
27 side of the Janus particle (green, III). The trajectories of the respective groups of passive beads are
28 shown in Figure 2a. The corresponding mean square displacement (MSD) curves are summarized
29 in Figure 2b. Those passive beads, which are affected by the strongest repulsion (red labelled)
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3 acquire the average MSD of about $1.85 \mu\text{m}^2$ in 4 s, which is higher compared to the beads at the
4 sides (blue labelled, $1.48 \mu\text{m}^2$ in 4 s) and the layers behind the cap (green labelled, $0.93 \mu\text{m}^2$ in 4 s).
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8 Due to specificity of the chemical reaction at the surface of the cap, the exclusion effect is time
9 dependent.⁵⁴ To quantify this effect, we calculate the time evolution of the exclusion area around
10 the Janus particle, which does not contain passive beads. As shown in Figure 2c, the area rapidly
11 increases to $195 \mu\text{m}^2$ after the initial 1.75 s, and reaches a maximum of $266 \mu\text{m}^2$ at 5.25 s, and then
12 decreases gradually to $29 \mu\text{m}^2$ over the next 40 s. To understand this behavior, we analyzed the
13 time-dependent radial distance between the Janus particle (located at the origin point of Figure 2d
14 and 2e, the orientation of the cap indicated with a black arrow) and the nearest layers of passive
15 beads. In addition, Figures 2d and 2e provide the angular distribution of the exclusion distance and
16 demonstrate that the strongest repulsion is observed in front of the Ag/AgCl cap, where the
17 concentration of the reaction products is expected to be highest. As shown in Figure 2f, the distance
18 between the cap of the Janus particle and passive beads assigned to the “red” group is 11.0 ± 1.1
19 μm . At the sides (blue group) the distance is smaller than $9.3 \pm 1.4 \mu\text{m}$. The smallest distance of
20 $6.7 \pm 0.6 \mu\text{m}$ is found between the Janus particle and those beads which belong to the “green”
21 group facing the PS side of the particle. Similar to the exclusion area, these distances change with
22 time: the distance significantly increases to its maximum value at around 6 s followed by a
23 monotonous decrease during the next 40 s.
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45 The data shows that the onset of the photocatalytic reaction (when the blue light is turned on)
46 initiates the exclusion behavior. With the illumination time, there will be an asymmetry in the
47 spatial profile of the concentration of protons and Cl⁻ ions around the Janus particle. The highest
48 concentration of the reaction products is in front of the Ag/AgCl cap, leading to the formation of
49 the observed asymmetry in the *radius of exclusion* around the Janus particle. This asymmetry in
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3 the interaction process is visible only due to the presence of the confining matrix where the passive
4 beads of the first several layers (closest to the Janus particle) cannot leave the interaction area.
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6 After about 6 s, the reaction rate starts to decrease and passive beads tend to move back closer to
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8 the location of the Janus particle.
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12 To further explore the asymmetric exclusion process, we performed numerical simulations of
13 the system. While the flow distribution around a Janus particle can be calculated for a simple case
14 of a single Janus particle in free space⁵⁶ or near a planar wall⁵⁷, the far-flow models are inapplicable
15 for a Janus particle embedded in a dense matrix. On the other hand, considering the environment
16 to be homogeneous on a large scale ($\gg d$), simple models of a flow distribution around a Janus
17 particle can be applied. This model is presented in the Methods section. We consider an
18 asymmetric flow parameter $\gamma(\theta)$, which is essentially a function of the direction with respect to
19 the axis of the Janus particle. To do so, we assume that the flow strength $\gamma(\theta)$ decreases from the
20 maximum value γ_{max} in front of the cap to the minimum value γ_{min} on the opposite side of the Janus
21 particle (facing its PS side), where $0 \leq \gamma_{min} < \gamma_{max}$. The asymmetric flow strength is modeled by a
22 function $\gamma_{sym} + \gamma_z$, where γ_{sym} is the symmetric part, and γ_z is an "anisotropy parameter" ($0 < \gamma_z$
23 $< \gamma_{max}$) that introduces a shift in the interaction between a Janus particle and a passive bead, along
24 the direction of the cap. Note that the flow of the reaction products around the Janus particle is
25 influenced by the presence of passive beads. However, the model used remains a good
26 approximation even in the case of a dense matrix of surrounding passive beads, due to the
27 following considerations: (1) The experimental setup is three-dimensional and the beads do not
28 block the flow but rather channel it in the gaps between the beads, and also above the beads. (2)
29 The impact of the dense matrix of passive beads on the flow is expected to be maximal when the
30 front of the flow reaches the inner shell of passive beads surrounding the Janus particle. In the next
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3 moment after that, the flow pushes the passive beads of the inner shell away from the Janus particle
4 and away from each other thus opening gaps between the beads such that the flow can further
5 proliferate through the arrays of the passive beads. This allows us to approximate the flow between
6 the beads as rather "homogeneous", on average (as passive beads are randomly positioned around
7 the Janus particle). (3) The flow decays with the distance from the Janus particle rapidly, which
8 means that the main impact of the flow is exerted on the inner shell of passive beads (as also
9 follows from our measurements and calculations of the MSD). Other passive beads (behind the
10 inner shell) are initially repelled due to the core-to-core interaction with the beads of the inner shell
11 rather than by the flow. After that, when the flow penetrates through the gaps between the beads
12 of the inner shell, other passive beads are carried by this flow.

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26 The simulated time evolution of the distributions of passive beads and their trajectories are
27 shown in Figure 3a for the time interval when the Janus particle is active: From the initial
28 configuration right after the blue light is turned on at $t = 0.001$ s (the passive beads are shown by
29 grey circles), to $t = 5$ s (blue circles) corresponding to the time when the maximum size of the
30 exclusion area is achieved in simulations. The trajectories of the beads are shown by dark blue
31 dotted lines. Similar to the approach to analyze the experimental data (Figure 2), we track
32 separately the simulated trajectories for the beads in front of the Janus particle (red dotted lines in
33 Figure 3b), at the sides (blue dotted lines) and behind the Janus particle (green dotted lines). The
34 averaged MSD curves for beads belonging to each of the three groups are shown in Figure 3(c).
35 The detailed analysis of all simulated MSD curves is given in Figure S4. Similar to the
36 experimental data presented in Figure 2b, the MSD analysis indicates a pronounced anisotropy of
37 the exclusion process. The larger MSD values in the simulations as compared to the experiment
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3 are explained by the ability of passive beads to freely move while in the experiment they
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5 experience a stronger pressure from the dense surrounding matrix.
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10 **Active Janus particle can perform rotational but no translational motion**

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12 Even more striking behavior is observed, when a photocatalytic active Janus particle can perform
13 rotational fluctuations without translational motion. In this case, depending on the interaction
14 between Janus particles and a substrate, we can expect distinct scenarios, spanning from the
15 diffusive to even subdiffusive rotational motion. The dense passive matrix should be able to
16 “detect” and follow the reorientation of the photocatalytic cap of the Janus particles overtime. In
17 the following, we realize this scenario and study the trajectories of the rotating Ag/AgCl Janus
18 particles and its interaction with the passive matrix via the analysis of the trajectories and angular
19 distribution of passive colloids in time (Figure 4a-d, Video S2). In this experiment, the density of
20 passive beads is 0.136 particles/ μm^2 (Figure S5). The Janus particle shows a noticeable rotational
21 movement (Figure 4e). Similar to the previous case of an immobile Janus particle, we split the area
22 around the Janus particle into *four regions* (Figure 4a). The regions correspond to the location of
23 passive beads with respect to the cap of the Janus particle *at the initial time*. The color coding is
24 as follows: in front of the cap (red, I), at the left side of the particle (blue, II), at the back side of
25 the particle facing its PS side (green, III) and at the right side of the particle (light blue, IV). The
26 trajectories of the Janus particle and passive beads and the corresponding MSD curves are
27 presented in Figure S6a and S6b, respectively. Due to the asymmetry in the repulsive particle-bead
28 interaction, the rotation of the Janus particle leads to the redistribution of passive beads in time
29 (Figure S7 and S8). The beads, which were assigned to the red group, were the first to respond to
30 the repulsion driven by the photocatalytic reaction. The exclusion area increased significantly
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3 during the first 3 s (Figure S6c). We calculated the distance from the Janus particle to the first
4 layer of passive beads (Figure 4f and 4g, see also Figure S7) and correlated this data to the
5 corresponding angular orientation of the cap of the Janus particle as a function of time (compare
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7 Figure 4e and 4h). In contrast to the data shown in Figure 2f (where the Janus particle is immobile)
8 revealing a monotonous decay of the exclusion distance with time, the distances in Figure 4h
9 display a multi-peak behavior, which is in line with the reorientation of the cap over the interaction
10 process. The average distance as a function of time reaches a peak value at 1.4 s and then decreases
11 during 10 s. The peak value is relatively small, due to the fact that the cap points toward the red-
12 colored group of particles (region I) for a very short time, of less than 1 s. After this time, the cap
13 starts to rotate toward the blue-colored group of particles (region II). The average distance reaches
14 its maximum of 11.8 μm at 1.75 s. Then the cap oscillates between the locations pointing toward
15 the green group (III) and light blue group (IV). Here, the distances between the Janus particle and
16 passive beads assigned to the green and light blue groups reach a maximum of 13.5 μm at 4.9 s
17 and 9.3 μm at 3.85 s, respectively. During the next 10 s, the cap remains oriented towards the beads
18 of the green group leading to the largest exclusion radius.

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38 To provide a deeper insight in the effect of a dense matrix on the rotational diffusion of a Janus
39 particle, we perform simulations of a system with a rotating Janus particle surrounded by a dense
40 matrix of passive beads. Snapshots revealing the time evolution of the distribution of passive beads
41 from the moment when the blue light is turned on to $t = 5$ s are summarized in Figure 5a-d. To
42 demonstrate the evolution between the consecutive time steps, we plot the current particle
43 distribution (green circles) and that at the previous time step (grey circles). The angular orientation
44 of the Janus particle is shown for each snapshot by a red arrow for the current time and by a grey
45 arrow for the previous time step. The analysis of the data shown in Figure 5a-d reveals that the
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3 shape of the exclusion area changes depending on the angular position of the cap of the Janus
4 particle. In the case when the rotation of the Janus particle is fast enough, we observe a rather
5 isotropic exclusion area (Figure 5d). Still, at each step the distribution of passive beads is clearly
6 anisotropic. The observed behavior indicates that the reorientation of the Janus particle is
7 associated with an angular redistribution of passive beads following the orientation of the cap of
8 the Janus particle. Therefore, the rotation inside a passive matrix induces a translational motion of
9 passive beads, which should be affected by the density of beads in the matrix. To address this
10 aspect, we simulate the time evolution of the angular orientation of the Janus particle during the
11 exclusion process in the case when the matrix possesses different density of passive beads, n_{pb}
12 (Figure 5e). While at low densities, the Janus particle executes fast rotations in both directions (the
13 $\theta(t)$ curves for $n_{pb} = 0.162$ and 0.321 particles/ μm^2), these changes become smoother when
14 increasing the density of the matrix ($n_{pb} = 0.509$ particles/ μm^2). In the latter case, sudden changes
15 of the direction of the Janus particle disappear and the angle evolves almost monotonically in one
16 direction. To assess if this behavior is an indication on the crossover to a subdiffusive regime, we
17 perform simulations of the time evolution of the angular orientation of a Janus particle accounting
18 for different rotational diffusion coefficients (Figure 5f): $D_r = 0.32$ rad²/s, 0.16 rad²/s, 0.08 rad²/s,
19 and 0.03 rad²/s, simulated for a matrix with the density of passive beads of $n_{pb} = 0.509$ particles/ μm^2 .
20 With the brown solid line we show the experimentally measured angular displacement of the Janus
21 particle. The simulation results are in quantitative agreement with the experiment. The
22 corresponding mean squared angular displacement (MSAD) curves are presented in Figure 5g.
23 Although with an increase of the density of the surrounding passive matrix, fast changes of the
24 orientation of the Janus particle become less pronounced, all the simulated MSAD curves show a
25 conventional rotational-diffusion behavior with a slope equal to one. The diffusion regimes are
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3 robust, and to observe a crossover to a subdiffusive regime or even the total suppression of the
4 rotational diffusion (or "directional locking"³²) a Janus particle should be embedded in a very dense,
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6 near-crystalline, or glassy matrix.
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10 11 12 **CONCLUSIONS**

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14 To summarize, we quantitatively investigate the repulsive behavior between immobile yet
15 photocatalytic Ag/AgCl capped Janus particles embedded in a dense matrix of passive silica beads
16 in pure water. As a result of the photocatalytic reaction, passive beads are repelled away from
17 active Janus particles. The exclusion effect is found to be stronger for those passive beads, which
18 are located in front of the Ag/AgCl cap of the Janus particle. This effect is interpreted in terms of
19 a stronger flow of the products of the chemical reaction from the photocatalytic cap. The profile
20 of the flow is visualized by tracking trajectories of passive beads. The study includes the analysis
21 of the MSD of passive beads as well as average distances from individual passive beads to the
22 Janus particle. Our conclusion is further supported by the investigation of dynamics in a dense soft
23 matter system containing Janus particles, which can perform rotational but no translational motion.
24 The rotation of the Janus particles results in a redistribution of passive beads according to the
25 angular orientation of the Ag/AgCl cap. We expect that our results will be helpful for a deeper
26 understanding of complex interactions between active and passive particles in various soft matter
27 systems, including those containing synthetic and biological active microswimmers like sperm
28 cell, algae, bacterial or motor proteins.
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51 **ASSOCIATED CONTENT**

52 **Supporting Information.**

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3 Supporting Information (file type: PDF): The file includes further details on the data analysis
4 including temporal evolution of the positions of passive beads and Janus particles, analysis of the
5 MSD and calculation of the density of passive beads in the matrix.
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10 Video S1 (file type: AVI): The video shows interactions in a soft matter system containing an
11 immobile Janus particle embedded in a dense matrix of passive SiO₂ beads.
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16 Video S2 (file type: AVI): The video shows interactions in a soft matter system containing a Janus
17 particle, which can perform rotational but no translational motion, embedded in a dense matrix of
18 passive SiO₂ beads.
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23 24 25 26 AUTHOR INFORMATION

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34 35 **Author Contributions**

36
37 LB and TH formulated the task. TH carried out experimental work with the contribution from SG,
38 XW, JS, and LB. VRM performed simulations and analyzed the data with contributions from FN
39 and WDM. The manuscript was written by LB, DM and VRM with contributions from TH, GC,
40 JF, WDM, FN. All authors have given approval to the final version of the manuscript.
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23 24 **Notes**

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27 The authors declare no competing financial interest.

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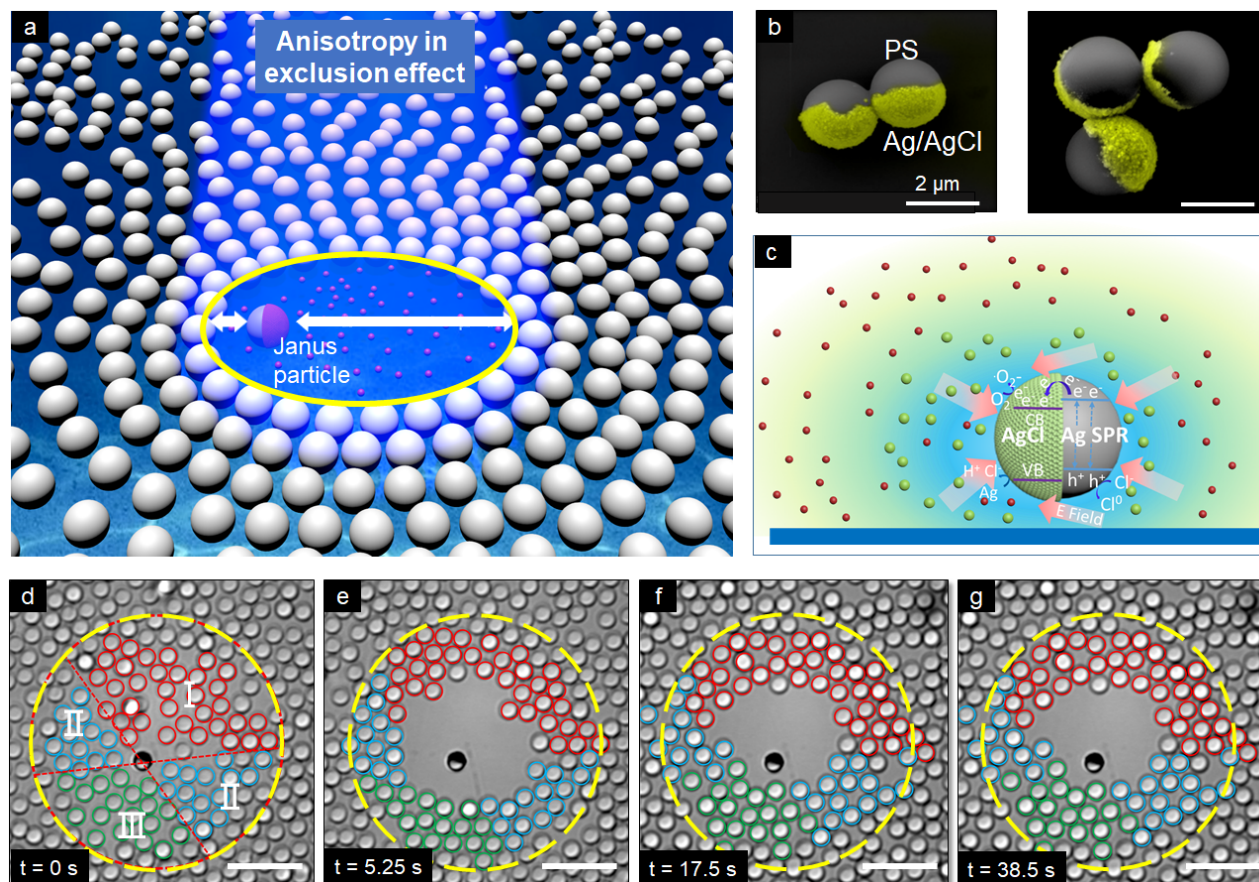


Figure 1. (a) Schematics of the asymmetry in the particle-bead repulsion in a soft-matter system containing an immobilized yet photocatalytically active Janus particle in a dense matrix of passive beads. (b) Scanning electron microscopy (SEM) image of a polystyrene (PS) based Janus particle with its Ag/AgCl cap shown with false color. Scale bar, 2 μm . (c) Schematics of the process when the SPR assisted absorption of visible light by the Ag/AgCl cap of a Janus particle results in a release of ions. Green and red dots depict protons and chlorine ions, respectively. Protons can diffuse faster than chlorine ions, forming a charged area in front of the cap. Pink arrows designate the orientation of the electric field around the Janus particle, oriented inward the cap. (d-g) A sequence of optical microscopy images showing the time evolution of the system of an immobile Janus particle interacting with the surrounding dense passive matrix (SiO_2 beads) under blue light illumination. For the analysis of the distribution of beads we define three relevant areas indicated

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3 in red (in front of the cap of the Janus particle), in green (behind the Janus particle facing its PS
4 side) and in blue (from both sides of the Janus particle). The images are frames of the Video S1.
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7 The anisotropy in the particle-bead repulsive interaction leads to the anisotropy in the shape of the
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10 exclusion area around the Janus particle. Scale bar, 10 μm .
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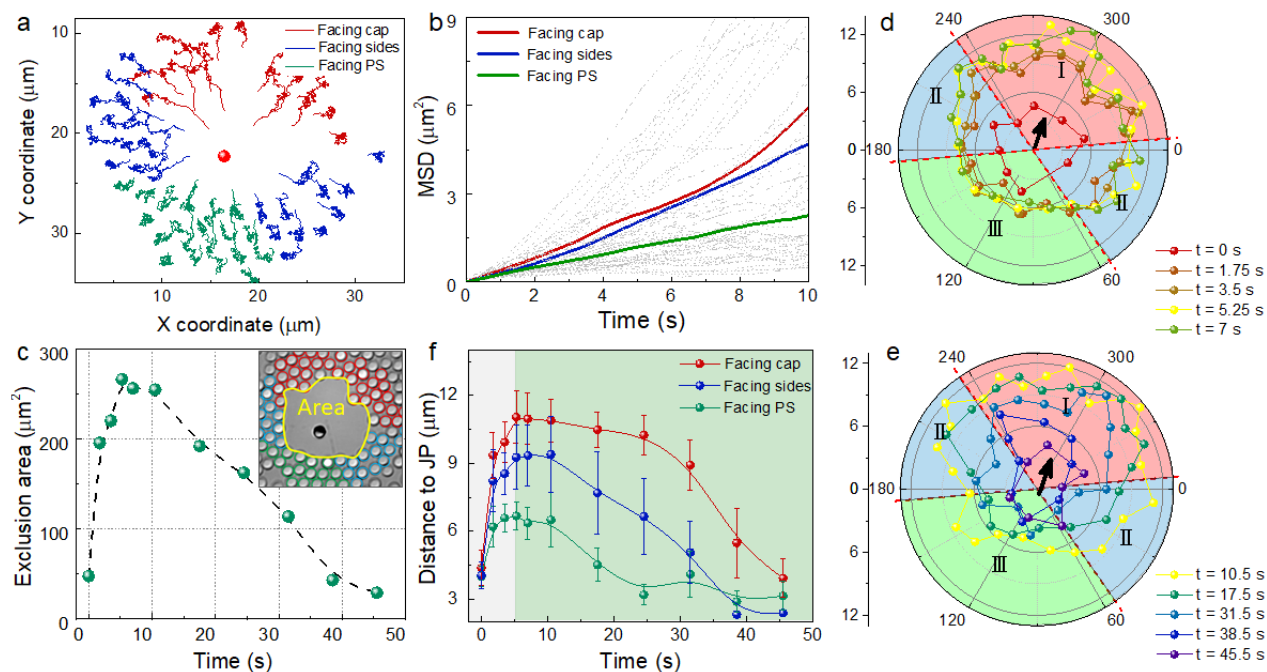


Figure 2. Experimental study of the interaction process in a system containing an immobile Janus particle and passive beads under blue light illumination. (a) Trajectories of passive beads, which are coded accordingly to the color scheme introduced in Figure 1d, *i.e.* accounting for the initial location of a passive bead with respect to the orientation of the cap of the Janus particle. (b) The corresponding MSD curves for all tracked passive beads (gray lines). The MSD curves shown with red, blue and green color are the result of averaging over all MSD curves taken of the beads belonging to one of the three groups. (c) The time evolution of the exclusion area. The insert demonstrates one of the snapshots of the Video S1 (illumination for 5.25 s), with the exclusion area indicated by a yellow line. Scale bar, 4 μm . (d, e) The time evolution of the distance between a Janus particle and the first layer of passive beads. The Janus particle is located in the center of the graph and the orientation of the main symmetry axis of the cap is indicated with the black arrow. (f) The time evolution of the average distance between a Janus particle and the first layer of passive beads. The averaging is carried out over all passive beads belonging to the indicated region color coded in red, blue, or green in the panels (d) and (e).

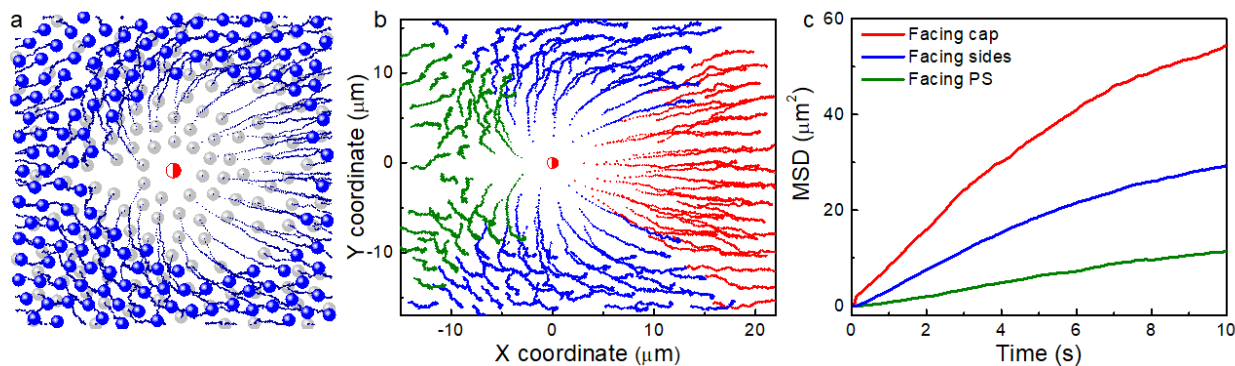


Figure 3. Theoretical study of the interaction process in a system containing an immobile Janus particle and passive beads. (a) Two overlaid snapshots from the simulation data revealing a distribution of passive beads right after blue light is turned on ($t = 0.001$ s; grey circles) and after illumination for 5 s (blue circles). Trajectories of passive beads are shown by dotted lines. (b) Trajectories of passive beads, which are coded accordingly to the color scheme introduced in Figure 1d, *i.e.* accounting for the initial location of a passive bead with respect to the orientation of the cap of the Janus particle: in front of the cap of the Janus particle (red dotted lines), on the sides (blue dotted lines), and behind the Janus particle facing its PS side (green dotted lines). (c) MSD curves shown with red, blue and green color are the result of averaging over all MSD curves taken of the beads belonging to one of the three groups. Further details are summarized in Figure S4.

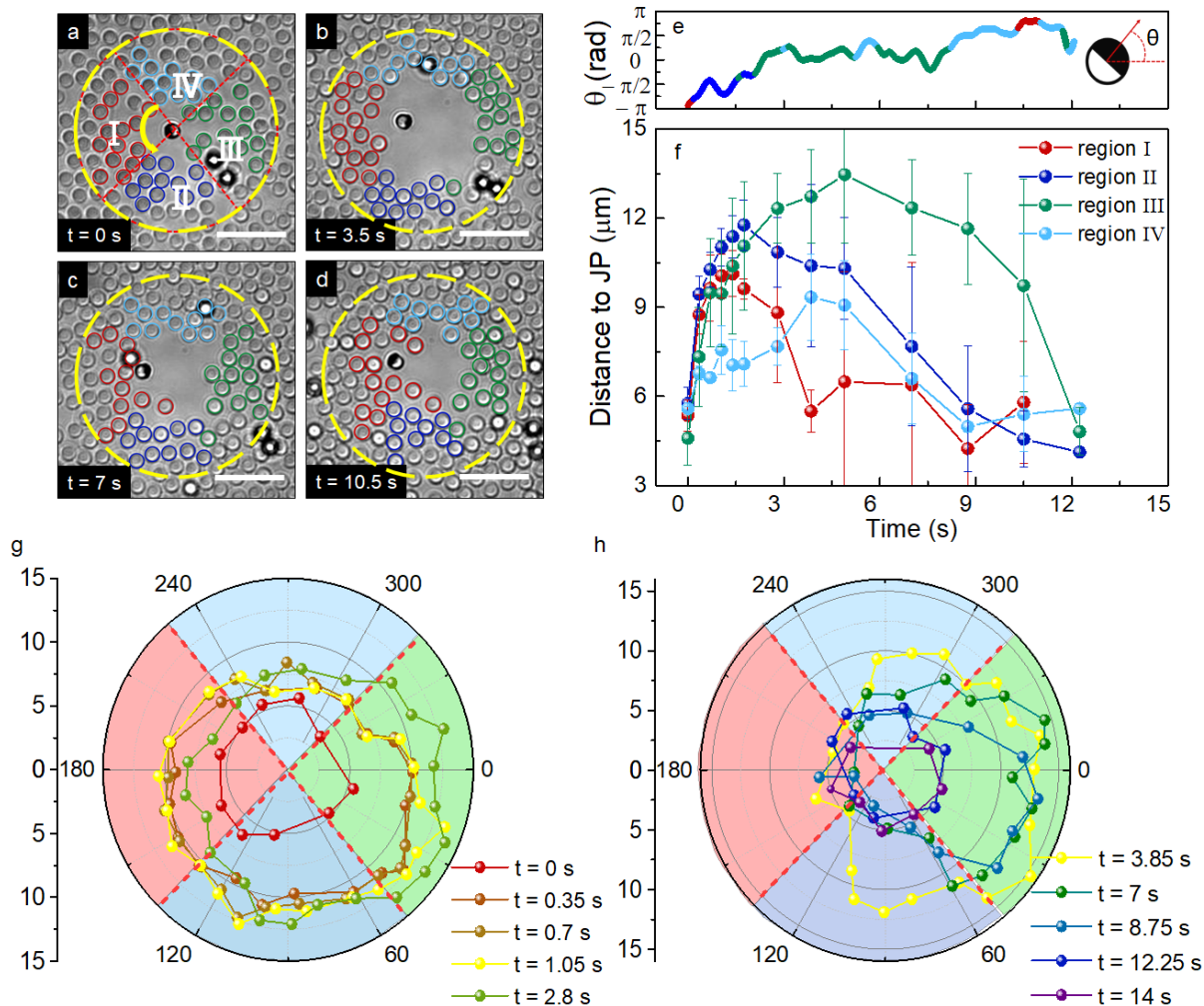


Figure 4. Experimental study of the interaction process in a system containing passive beads and a Janus particle, which can perform rotational but no translational motion, under blue light illumination. (a-d) A sequence of optical microscopy images showing the time evolution of the system. For the analysis of the distribution of beads, we define four relevant areas indicated in red (in front of the cap of the Janus particle), in green (behind the Janus particle facing its PS side), blue (at the left side of the Janus particle), and light blue (at the right side of the Janus particle). The images are frames of the Video S2. Scale bar, 10 μm . (e) The time evolution of the angular orientation of the cap of the Janus particle. The curve is color coded to indicate the orientation of the cap with respect to the location of the initially-assigned groups of passive beads. (f, g) The

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3 time evolution of the distance between a Janus particle and the first layer of passive beads. The
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5 Janus particle is located in the center of the graph and the orientation of the main symmetry axis
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7 of the cap is shown in panel (e). (h) The time evolution of the average distance between the Janus
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9 particle and the first layer of passive beads. The averaging is carried out over all passive beads
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11 belonging to the indicated region color coded in red, green, blue or light blue in the panel (f) and
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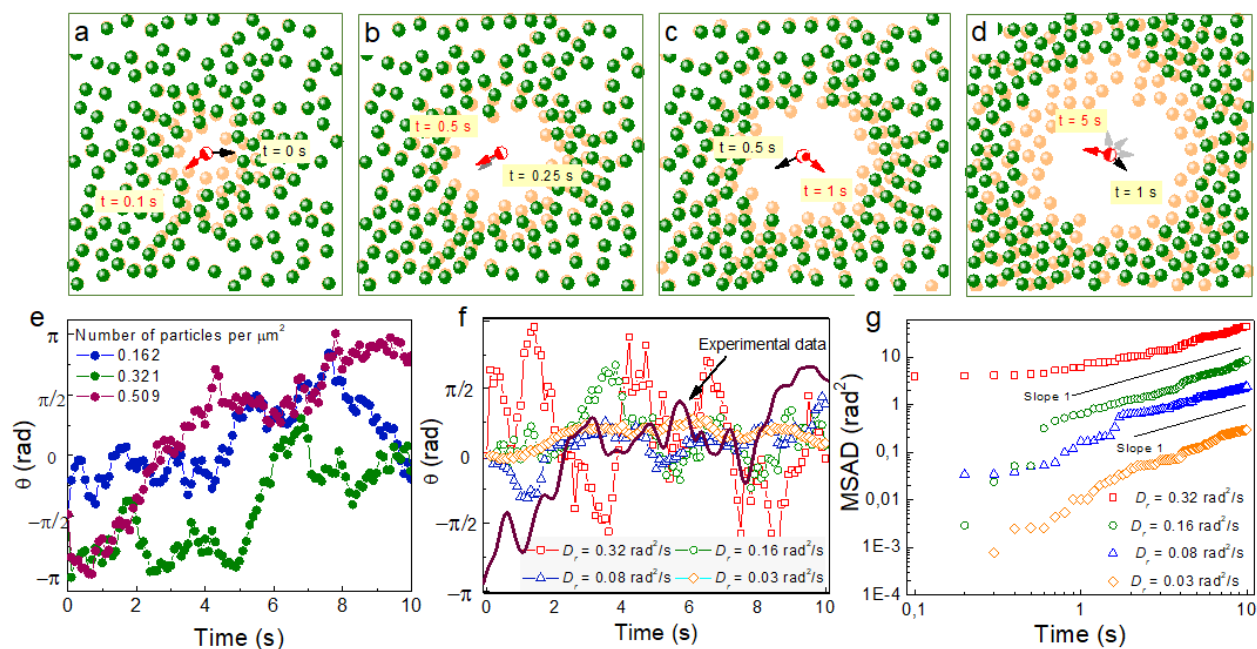


Figure 5. Theoretical study of the interaction process in a system containing passive beads and a Janus particle, which can perform rotational but no translational motion. (a-d) The time evolution of the interacting system after the blue light is turned on. The snapshots are taken at $t = 0.1$ s (a), 0.5 s (b), 1 s (c), and 5 s (d) for the density of passive beads, n_{pb} , of 0.509 particles/ μm^2 . The distribution of passive beads at the previous time step is shown in each panel with orange circles. The Janus particle in the center is shown with a half-filled red circle and its orientation is indicated with a red arrow (grey arrow for the previous time step). (e) The time evolution of the angular orientation of the cap of the Janus particle, $\theta(t)$, for a matrix with different densities of passive beads, $n_{pb} = 0.162, 0.321$ and 0.509 particles/ μm^2 . (f) The time evolution of the angular orientation of a Janus particle possessing different rotational diffusion coefficients: $D_r = 0.32$ rad²/s, 0.16 rad²/s, 0.08 rad²/s and 0.03 rad²/s. The brown solid line shows the experimentally measured angular displacement of the Janus particle. (g) The corresponding mean squared angular displacement (MSAD) curves. The straight lines show the slope corresponding to a conventional rotational diffusion.

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